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Title:

NON-VOLATILE ZERO FIELD SPLITTING RESONANCE MEMORY

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NON-VOLATILE ZERO FIELD SPLITTING RESONANCE MEMORY

[0001] The invention disclosed in this application is related to the invention disclosed by U.S. patent application _____ (Attorney Docket No. M4065.1009/P1009), filed concurrently with this application by Kristy A. Campbell and Terry L. Gilton. The entirety of this related application is hereby incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The invention relates to memory devices utilizing zero field splitting parameters and methods of making and using such memory devices.

BACKGROUND

[0003] Integrated circuit designers have always sought the ideal semiconductor memory: a device that is randomly accessible, can be written or read very quickly, is non-volatile, but indefinitely alterable, consumes little power, and is scalable. The search for such devices has led to investigations into atomic-level properties of materials for switching and memory applications.

[0004] Studies have been conducted into electron spin transistors and memory components. Even in the absence of a magnetic field, some metal ions exhibit splitting of the electron spin energy levels. This is referred to as zero field splitting. Zero field splitting is different from Zeeman splitting (i.e., separation of the electron spin energy levels in the presence of an externally applied magnetic field). The difference being that some molecules may exhibit splitting of the electron energy levels at zero externally applied magnetic field, due in part, to the natural crystal fields present around a metal ion (in the case of molecules with transition metal ions) or to spin-spin coupling within a molecule or between molecules. Molecules with transition metals (e.g., Mn, V, Fe, Co, Cr, Ni, Cu, Zn, Cd, and others) are quite frequently paramagnetic and may have electron spin energy levels at zero magnetic field with an energy splitting between levels for which a spin transition is allowed that is within a range detectable with microwave radiation. For example, as shown in FIG. 1, Mn^{+3} ions have a spin system with an effective spin $S = 2$, with a positive zero field splitting value. The inset portion of FIG. 1 is an expanded view of the $Ms = \pm 2$ energy levels in the region of observed parallel mode electron paramagnetic resonance transitions (indicated by the double arrows). Analytical techniques, such as microwave

spectroscopy or electron paramagnetic resonance (EPR) spectroscopy can identify molecular systems that exhibit zero field splitting properties.

[0005] Spin-spin interactions occur when there is at least one unpaired electron interacting with another unpaired electron (S greater than or equal to 1, where S is the effective spin). An example molecular system that could give rise to this situation includes a molecule containing Mn^{+3}, which has a total spin $S = 2$ (e.g., the molecule Mn(salen)). In this case, there are 4 unpaired electrons interacting with each other.

[0006] Microwave absorption spectroscopy has been used to identify atomic properties of chemical species. Microwave absorption has been shown to be a viable means of determining energy absorption at frequencies corresponding to the zero field splitting value of the absorbing material.

[0007] It would be advantageous to utilize the zero field splitting properties of ions as a memory device. It would be additionally advantageous if such a memory device was non-volatile or semi-volatile, operated at speeds necessary for present memory functions, and could be scaled to sub-micron sizes.

SUMMARY

[0008] An exemplary embodiment of the invention provides a low-volatility or non-volatile memory cell utilizing the zero field splitting properties of a material to store data. The memory cell may incorporate at least one transition metal ion species. In response to an energy pulse, e.g., electrical or optical, the host material can switch between energy absorbing and non-energy absorbing (or less energy absorbing) states based on the zero field splitting properties of the material induced by the applied signal. Exemplary host material and metal ion combinations include chalcogenide glass with manganese ions, standard float glass (e.g., Na_2O-CaO-MgO-SiO_2) with ions (e.g., Mn ions), perovskite (e.g., $CaTiO_3$ and $MgSiO_3$) materials with manganese ions, porphyrins with manganese or zinc, or ferrocenes with ion species.

[0009] Another exemplary embodiment of the invention provides a memory cell, which can store multiple bits of data using a plurality of metal ion species in a single host material.

[0010] These and other features of exemplary embodiments of the invention will be more apparent from the following detailed description and drawings which illustrate the various embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is an energy level diagram of an $S = 2$ system illustrating zero field splitting for a transition metal ion species.

[0012] FIG. 2 is an illustration of a cross-section of a memory cell in accordance with an exemplary embodiment of the invention;

[0013] FIG. 3 is a graph showing the low field signal where zero field splitting may be observed in an exemplary embodiment of the invention;

[0014] FIG. 4 is a representative portion of a memory array incorporating memory cells in accordance with the invention; and

[0015] FIG. 5 is a representation of a processor system employing a memory device incorporating exemplary embodiments of memory cells in accordance with the invention.

DETAILED DESCRIPTION

[0016] In the following detailed description, reference is made to the accompanying drawings, which are a part of the specification, and in which is shown by way of illustration various embodiments whereby the invention may be practiced. These embodiments are described in sufficient detail to

enable those skilled in the art to make and use the invention. It is to be understood that other embodiments may be utilized, and that structural, logical, and electrical changes, as well as changes in the materials used, may be made without departing from the spirit and scope of the present invention. Additionally, certain processing steps are described and a particular order of processing steps is disclosed; however, the sequence of steps is not limited to that set forth herein and may be changed as is known in the art, with the exception of steps or acts necessarily occurring in a certain order.

[0017] The terms "wafer" and "substrate" are to be understood as interchangeable and as including any foundation suitable for supporting a memory element of the invention. For example, the substrate can be silicon, silicon-on-insulator (SOI), silicon-on-sapphire (SOS), doped and undoped semiconductors, epitaxial layers of silicon supported by a base semiconductor foundation, and other semiconductor, conductor, or insulator structures. Furthermore, when reference is made to a "wafer" or "substrate" in the following description, previous process steps may have been utilized to form regions, junctions or material layers in or on the base structure or foundation. In addition, the semiconductor substrate need not be silicon-based, but could be based on silicon-germanium, germanium, gallium arsenide, or other known semiconductor materials. Further, the substrate need not be

semiconductor-based at all, but can be any material suitable for supporting an integrated circuit memory structure, for instance, polymer, glass, metals, insulated metals, ceramics, and other materials.

[0018] The invention utilizes zero field splitting (ZFS) properties of certain metal ions to form a memory cell. Transition metal ions, such as ions of Co, Cr, Fe, Mn, Ti, Cu, Zn, V, Cd, and Ni, and others, are preferred and can be added to a host material, such as an organic molecular matrix or an inorganic matrix. The selection of the metal ions and the host material determines the zero field splitting energy; the host material may or may not play a role in the zero field splitting properties of the ions in memory operation. The selection of these ions and host materials should result in microwave absorption energies of about 0.03 cm^{-1} to 3.3 cm^{-1} at zero field to satisfy requirements for memory state sensing.

[0019] The separation of spin states in the metal ions within the host material at zero magnetic field should be be small enough to be able to utilize the energy available on a standard semiconductor chip. The host material, if organic, can be polymer based or porphyrin based. If the host material is inorganic, it may be a chalcogenide glass, e.g., arsenic selenide or germanium selenide, a semiconductor, or a silicate, for example.

[0020] Now referring to the figures, where like reference numbers designate like elements, FIG. 2 shows a simplified illustration of a specific memory cell construction in accordance with an exemplary embodiment of the invention. The memory cell 10 is shown as supported by a substrate 12, which may be silicon-based, but as indicated above, the substrate can be any of a number of materials. The substrate 12 can be formed or provided as is known in the art by conventional means, depending on its composition.

[0021] An optional insulating layer 14 is provided over the substrate 12 if it is semiconductor-based. The optional insulating layer 14 can be, for example, silicon oxide or silicon nitride, and can be formed by CVD (chemical vapor deposition), sputtering, oxidation of the substrate 12, or other known techniques.

[0022] Over the optional insulating layer 14, or substrate 12 if that layer 14 is excluded, is provided an electrode 16 of a conductive material. The conductive material for the electrode 16 can be any of a number of materials, including, but not limited to, tungsten, tungsten nitride, aluminum, copper, doped polysilicon, nickel, titanium, and platinum. The electrode 16 material can be deposited by CVD, PECVD (plasma enhanced chemical vapor deposition), sputtering, plating, or other known techniques, and the electrode 16 can thereafter be defined by patterning and etching, if desired.

[0023] Over and electrically coupled to the electrode 18 is deposited a layer of host material 18, which incorporates metal ions, such as Mn^{+2}, for example. The host material 18 can be an organic or inorganic molecular matrix (as indicated above) and can be formed by blanket deposition techniques, which may be followed by patterning and etching if desired, or, alternatively, may be formed by an in-via process; either deposition process may include CVD, sputtering, co-sputtering, thermal evaporation, or other known techniques. The host material 18 can be about 100 Å to about 2,000 Å thick.

[0024] For example, one suitable and exemplary host material 18 is a Ge_xSe_{100-x} glass, for example, a $Ge_{40}Se_{60}$ glass. Preferably, the glass and ions (e.g., Mn^{+2} ions, which may be provided as MnSe) are deposited together by cosputtering or co-evaporation. In another method, the glass is first deposited, for example, by sputtering, and then a layer of ions is formed over the $Ge_{40}Se_{60}$ host material 18, for example, by sputtering or thermal evaporation. The ions can be incorporated into the host material 18 by photodoping or thermal diffusion, or by other means. If the host material 18 itself exhibits zero field splitting properties, the step of adding ions may be omitted.

[0025] Depending on the selection of host material 18 and metal ion pairing, the host material 18 can incorporate from less than about 0.3% to up to about 10% (by weight) metal ions. About 1 wt. % ion concentration is preferred.

[0026] A second electrode 20 is next deposited over the ion-doped host material 18. The second electrode 20 can be of the same or similar materials as the first electrode 16 and can be formed by the same or similar techniques. The memory device 10 stack can be surrounded by an insulating material 22, such as BPSG (borophosphosilicate glass) or polyimide, and the wafer can be planarized by CMP (chemical mechanical polishing) using the top electrode 20 as a stop, if desired. The memory device 10 shown in FIG. 2 is representative of one of a plurality of such devices that can be arranged in a memory array.

[0027] The Mn^{+2} ions in the above-described exemplary $Ge_{40}Se_{60}$ glass enable the host material 18 to display a relatively large microwave absorption at zero field, which enables the device to store data as energy absorption states. A memory device in accordance with this exemplary embodiment can absorb about 0.33 cm^{-1} of energy of a potential pulse having a rise time of about 35 picoseconds and a frequency of about 9.68 GHz. As shown by the graph in FIG. 3, the zero field splitting absorption is observed at relatively low

field signal in the structure of this embodiment. The germanium selenide stoichiometry plays a role in the functioning of this exemplary cell, with the $Ge_{40}Se_{60}$ glass being preferred over other germanium selenide stoichiometries. Other glass types and stoichiometries can be used in the invention, however.

[0028] In the embodiment discussed in the preceding paragraphs in relation to FIG. 2, the first electrode 16 can comprise manganese. The second electrode 20 can be tungsten. These electrodes 16 and 20 are not limited to such materials, however. Other conductive materials such as doped polysilicon, titanium, aluminum, copper, silver, platinum, nickel, and conductive nitrides can be used as well.

[0029] Other combinations of metal ions and host materials 18 can also be used for a memory device in accordance with the invention. As previously indicated, such combinations should be able to absorb a detectable amount of energy when in a programmed state. For example, a standard float glass doped with less than about 1% Mn^{+2}, Mn^{+3}, or Fe^{+3} has been shown to absorb a detectable amount of energy in the microwave frequency range. Float glass can comprise Na_2O-CaO-MgO-SiO_2, and the metal ions can be incorporated into the glass as about 1 wt. % MnO_2 or Fe_2O_3. Additionally, borosilicate glasses doped with Cu, Ni, Co, and Fe in high concentrations (greater than about 10%) exhibit detectable non-resonant microwave absorption at zero

field. The energy absorption characteristics of these alternative host material/metal ion combinations at zero magnetic field have been known in the art, but never utilized as part of a memory device. Other examples of materials that could be engineered to contain transition metals that could be oxidized/reduced by applied potentials or light to exhibit zero field splitting memory behavior include porphyrins, ferrocenes, and perovskites.

[0030] As shown in FIG. 4, the memory cells 10 of the invention can be utilized in a memory array by being formed between conductive intersecting column lines 30 and row lines 32. At each intersection is located the host material 18 comprising metal ions. When the host material 18 is of the appropriate composition (e.g., the correct matrix material supporting the correct ions and ligands), it can be written, read, and erased in a non-volatile manner for operation as a memory device as discussed herein.

[0031] A memory cell in accordance with an exemplary embodiment of the invention stores information as a stable energy absorption state; which is one of two states, the other being a stable non-energy-absorbing state. The energy absorbing property of the memory cell should be sufficient to absorb a detectable amount of an energy (e.g., electrical or optical) impulse at a bandwidth corresponding to the splitting at zero field of the ions in the host material. Energy, bandwidth frequency, and pulse rise time are interrelated

variables relating to the programming of the memory cell. These variables are interrelated in general accordance with the following formulas:

$$\text{Bandwidth frequency (Hz)} \approx \frac{0.35}{\text{pulse rise time (seconds)}} \quad \ldots . (1a)$$

$$\text{Energy } (cm^{-1}) \approx \frac{\text{Bandwidth frequency (Hz)}}{3 \times 10^{10} \text{ (cm/s)}} \quad \ldots . (1b)$$

[0032] Although the two memory states of the memory cells of the invention have been described as an energy-absorbing state and a non-energy-absorbing state, the invention is not limited to such states. Two energy-absorbing states may also be used, where the amount of energy absorption each state exhibits is great enough for individual detection and also allows effective differentiation between the two states.

[0033] Writing (as well as erasing) the memory cells can be accomplished by three phenomena: (1) changing the oxidation state of the metal ions of the cell; (2) changing the ligand field environment of the metal ions; each induced either by using a voltage potential or light impulse; or (3) a combination of (1) and (2). Either of these inducement techniques can change the zero field splitting parameters of the metal ions in a host material 18.

[0034] The exemplary memory device of the invention can be written by a potential pulse as already discussed. For example, as shown in FIG. 4, a column line 30 is charged with a programming potential while an intersecting row line 32a is grounded. The memory cell 10a at the intersection of the column line 30 and row line 32a is then programmed (e.g., by redox reaction or ligand field change) to the stable energy-absorbing memory state from a stable non-energy-absorbing state.

[0035] The specific mechanism enabling the memory cell to switch between energy-absorbing and non-energy-absorbing states will vary depending upon the way the metal ion is altered. Examples include a change in oxidation state of the ions (e.g., Mn^{+2}) within the host material (e.g., $Ge_{40}Se_{60}$) or because of an alteration of the distribution of molecular species within the memory element of the device such that the metal ions are associated with a charged ligand field environment around the ion. Under the oxidation theory, the metal ions of the host material may form a redox pair, such as Mn^{+2}/Mn^{+3}, Cu^{+2}/Cu^{+1}, or Fe^{+2}/Fe^{+3}, which permits energy absorption within the cell. Under the altered ligand theory, the ligand field around the metal ions may undergo a structural change within the memory cell. For example, if a potential applied in a specific direction across the cell causes a rearrangement in the molecular matrix or if the metal ions

redistribute non-homogeneously and see more spin-spin interactions (electrons interacting with each other) due to ion proximity, energy absorption can be enabled or disabled within the cell.

[0036] Because the memory cell's ability to store data is based on a changeable physical property of the cell, the memory cell can be non-volatile, or at least has very low volatility compared with prior art memory technologies such as DRAM. For example, if the programming mechanism is based on a redox reaction, once the potential applied across the cell generates a larger distribution of one redox state of the metal ions, removal of the potential does not initiate a reverse redox reaction. Likewise, a rearrangement of the molecular matrix remains until another input of energy changes the matrix.

[0037] After programming, the memory device can be returned to its original energy absorption state. One method of turning off programmed devices is by applying a reverse voltage potential relative to the programming potential of the stimulation pulse. Another method is by utilizing a light pulse.

[0038] The programmed state of the memory cell can be read, preferably, by sensing the absorption or transmission of energy from a read electrical pulse applied to the cell. After programming a cell to an energy-

absorbing state, the metal ions of the cell have a zero field interaction, which results in the metal ions being able to absorb a detectable amount of energy corresponding to the splitting at zero field. If the pulse rise time corresponds to the separation in energy of the electron spin levels at zero field, the signal (or at least a detectable portion thereof) is absorbed by the memory cell and a reduced or absent energy transmission can be sensed by read circuitry. However, if no energy is absorbed because the cell is not programmed to an energy-absorbing state, the energy applied to the cell remains largely intact and can be sensed by read circuitry as corresponding to the non-programmed state of the cell.

[0039] The energy pulse rise time of the read signal is selected (in accordance with Equations (1a) and (1b)) so that a non-programmed cell does not affect the pulse, but a programmed cell absorbs at least a detectable amount of the transmitted energy. Pulse rise times are specific to the zero field splitting parameters of the molecular system. Pulse rise times in accordance with the exemplary embodiments of the invention (FIG. 2) described above should be about 380 picoseconds to less than 4 picoseconds in order to correspond to the separation in electron spin level energy at zero field of the metal ions used in the memory cells; Mn^{+2}, Cu^{+2}, and Fe^{+2} being

examples. The memory device's access speed is limited only by the speed of the access electronics.

[0040] A memory cell 10a can be addressed for reading by a read pulse input at the column line 30 (with row line 32a grounded). As the pulse propagates down the column line it is absorbed by the memory cell 10a host material 18 if: (1) the host material 18 is in a zero field splitting state; and (2) the row line 32a at the address is grounded. The memory cell 10a is read by sense circuitry 34 in electrical communication with the column line 30 according to the amount of the column line 30 pulse absorbed by the memory cell 10a.

[0041] In accordance with another embodiment of the invention, the memory cells 10 can be induced to change state by a light pulse. The light pulse may either make the cells permanently change state (e.g., to an energy-absorbing state) for a write-once device, or a second wavelength of light (or some other energy input) could reverse the state written by the first wavelength (e.g., to a non-energy-absorbing state), making for a non-volatile memory (e.g., random access memory). The light pulse can induce an oxidation state change in the memory cells 10. Physical changes in the glass matrix host material 18 system or molecular conformal changes may occur.

[0042] In another embodiment in accordance with the invention, the host material 18 incorporates multiple transition metal ion species (more than one ion type) to make a memory cell 10 having a multi-state zero field splitting resonance memory, which is capable of storing multiple bits. The basic structure of such a memory cell 10 can be like that shown in FIG. 2 and described above. However, where the host material 18 of the embodiment described in accordance with FIG. 2 is doped only with one metal ion species, the host material 18 of this embodiment incorporates at least two metal ion species, for example, one ion can be Mn^{+2} and another can be Cu^{+2}. Both can be incorporated in a $Ge_{40}Se_{60}$ host material.

[0043] This embodiment is capable of multiple oxidation states or multiple configurations which have different zero field splitting parameters. Because each transition metal ion (e.g., ions of Mn, Ti, Co, Cr, Cu, Zn, Ni, Fe, Cd, V, and others) has a different zero field splitting energy in the matrix, each programmed state relating to the different ion types can be accessed for a reading operation using a different electrical energy pulse with a rise time corresponding to the energy splitting of a particular ion. For example, a pulse corresponding to a zero field splitting energy of 0.35 cm^{-1} may be used to read a bit corresponding to Mn^{+3} ions, but a pulse of greater or lesser magnitude and different rise time may be used for reading a bit stored by Cu^{+2}, where the

latter pulse would have no effect on the bit stored by the Mn^{+3} ion because rise times are coordinated with the different ion species. A single memory cell 10 can therefore contain a plurality of independent memory states, which can each be independently read by changing the rise time of the read pulse. As with other embodiments discussed above, the memory cells 10 of this embodiment can be programmed by either application of a light pulse of a certain wavelength or by application of a potential across the memory cell 10. The ions of different metal species may respond to a programming input with either an oxidation state change or a ligand field rearrangement, as discussed.

[0044] In this embodiment, it is possible that programming for an ion species with a higher potential programming needs could affect the programmed state of an ion species with lower potential programming needs. Therefore, there should be an order in programming through the various ion species types that takes this into consideration. It is also possible to use various combinations of electrical and light pulses to program the memory cells. The reading of memory states would be independent because pulse rise times used for reading the various ions of a memory cell would be specific to individual ion types and would have no effect on other ion types since these rise times can be correlated to the zero field splitting energy.

[0045] FIG. 5 shows a typical processor-based system 400, which includes a memory circuit 448, for example, a programmable RAM, employing memory devices having memory cells 10 constructed in accordance with the invention. A processor system, such as computer system, generally comprises a central processing unit (CPU) 444, such as a microprocessor, a digital signal processor, or other programmable digital logic devices. Such devices communicate with an input/output (I/O) device 446 over a bus 452. The memory 448 communicates with the system over the bus 452, typically by a memory controller.

[0046] In the case of a computer system, the processor may include peripheral devices, such as a disk drive 454 and a CDROM drive 456, which also communicate with the CPU 444 over the bus 452. Memory 448 is preferably constructed as an integrated circuit, which includes one or more memory devices having memory cells 10. If desired, the memory 448 may be combined with the processor, for example CPU 444, in a single integrated circuit.

[0047] The processes and devices described above are merely illustrative of but a few of the preferred methods and devices that could be used and produced in accordance with the invention. The above description and drawings illustrate embodiments, which achieve the objects, features, and

advantages of the invention. However, it is not intended that the invention be strictly limited to the above-described and illustrated embodiments. Any modifications of the invention that come within the spirit and scope of the following claims should be considered part of the invention.

[0048] What is claimed as new and desired to be protected by Letters Patent of the United States is: